

**SPRAY CARRIER STABILITY, PLANT MOBILITY, AND RUNOFF  
POTENTIAL OF TRIFLOXYSULFURON**

A Dissertation

by

MARK ANDREW MATOCHA

Submitted to the Office of Graduate Studies of  
Texas A&M University  
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

August 2006

Major Subject: Agronomy

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## ABSTRACT

### Spray Carrier Stability, Plant Mobility, and Runoff Potential of Trifloxysulfuron. (August 2006)

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Chair of Advisory Committee: Dr. Scott A. Senseman

Trifloxysulfuron is a sulfonylurea herbicide developed for postemergence weed control in cotton, sugarcane, and turf. Greenhouse and laboratory studies were conducted at the Texas A&M University campus and at the USDA-ARS research facility in Stoneville, MS to: 1) quantify the dissipation of trifloxysulfuron in a spray tank at 0, 1, 3, 7, 14, and 21 d after mixing as influenced by pH of the spray carrier and evaluate the resulting effects on efficacy on Palmer amaranth (*Amaranthus palmeri* S. Wats); 2) determine the effect of spray carrier pH on absorption and translocation of radiolabeled trifloxysulfuron in Palmer amaranth and Texasweed (*Caperonia palustris* (L.) St. Hil.); 3) determine average edge-of-field concentrations, total mass losses, and fractional losses of trifloxysulfuron applied to cotton at the 5-leaf stage and to bare soil as influenced by simulated rainfall.

The dissipation of trifloxysulfuron followed first-order kinetics. Calculated half-life values indicated that hydrolysis occurred more rapidly with the more acidic spray carriers with little or no difference between neutral and alkaline pH levels. Bioassay on Palmer amaranth showed no differences in plant dry weights due to pH level or

dissipation time. The absorption of  $^{14}\text{C}$ -trifloxysulfuron was greater for Palmer amaranth than for Texasweed when averaged over time and pH. Altering pH did not affect the translocation of trifloxysulfuron in Palmer amaranth. In contrast, translocation of  $^{14}\text{C}$ -trifloxysulfuron in Texasweed increased in the order of  $\text{pH } 5 < \text{pH } 7 = \text{pH } 9$ . Cumulative trifloxysulfuron losses in runoff from cotton plots were  $0.21 \text{ g ha}^{-1}$  while losses from bare plots were  $0.13 \text{ g ha}^{-1}$ . These values corresponded to fractional losses of 2.7% for cotton plots and 1.7% for bare plots of the total amount applied. These studies provide important information regarding the stability, plant uptake, and runoff potential of a commonly used sulfonylurea herbicide.

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## CHAPTER I

### INTRODUCTION AND LITERATURE REVIEW

Texas leads the U.S. in cotton (*Gossypium hirsutum* L.) production. In 2004, Texas cotton growers planted 2.4 million ha of cotton. This exceeds 24,000 square km and a land area larger than Connecticut, Delaware and Rhode Island combined. Cotton is the leading cash crop of Texas and ranks only behind the beef and nursery industries in total cash receipts for the state. In any one year, Texas cotton growers produce between 4 and 6 million bales. This represents more than \$1 billion to the Texas economy and is between 25 and 30% of the entire U.S. crop.

Controlling weeds in Texas cotton is one of the most critical aspects of successful lint production. Excessive weed populations can deplete valuable moisture and nutrients from the crop as well as cause significant quality reductions at harvest. A critical challenge in cotton weed control is providing the seedling cotton plants with conditions that allow the crop to outgrow weeds, thus providing a height differential for directed sprays. Recent technological advancements have changed many aspects of weed control in cotton, but challenges will always be present.

One recent technological advancement includes the discovery of the sulfonylurea (SU) herbicides in the 1970's. There are approximately 25 different active ingredients

currently manufactured. SUs are used in a wide range of crops and vegetables including corn (*Zea mays* L.), sorghum (*Sorghum bicolor* (L.) Moench), cotton, soybean (*Glycine max*), rice (*Oryza sativa* L.), wheat (*Triticum aestivum* L.), watermelon (*Citrullus lanatus* (Thunb.) Matsum. & Nakai), tomato (*Lycopersicon esculentum* L.), sugarcane (*Saccharum* spp.), pasture, forestry, turf, and potatoes (*Solanum tuberosum* L.) (Sarmah and Sabadie 2002). SUs are applied at very low use rates, have high specific activity, and low environmental impact.

Due to their chemical properties, SUs have very low water solubility under certain conditions, specifically at low solution pH. In addition to reduced solubility, SUs are also subject to chemical hydrolysis while in aqueous solution. Reduced herbicide solubility could also affect the absorption and translocation of SU herbicides into plant leaves possibly decreasing herbicide efficacy. Additionally, decreased herbicide absorption could result in more herbicide remaining on the leaf surface that could potentially be washed off by rainfall.

Trifloxysulfuron (*N*-[(4,6-dimethoxy-2-pyrimidinyl)carbamoyl]-3-(2,2,2-trifluoroethoxy)-pyridin-2-sulfonamide sodium salt), the active ingredient in Envoke<sup>®</sup>, is a SU herbicide developed by Syngenta for postemergence (POST) weed control in cotton. Trifloxysulfuron has shown activity on sicklepod (*Senna obtusifolia* (L.) H.S. Irwin & Barneby), ivyleaf morningglory [*Ipomoea hederacea* (L.) Jacq.], pitted morningglory (*Ipomoea lacunosa* L.), yellow nutsedge (*Cyperus esculentus* L.), purple nutsedge (*Cyperus rotundus* L.), redroot pigweed (*Amaranthus retroflexus* L.), common lambsquarter, and seedling johnsongrass [*Sorghum halapense* (L.)] (Holloway et al.

2000; Hudetz et al. 2000). Trifloxysulfuron is one of two POST herbicides developed for broadleaf weed control that can be applied in conventional cotton without a high risk of crop injury, yield or quality reductions. However, due to its chemical structure it is possible that the activity and environmental fate of trifloxysulfuron may be influenced by spray carrier pH.

Trifloxysulfuron inhibits acetolactate synthase (ALS) in susceptible plants (Hudetz et al. 2000). The SUs inhibit the production of the ALS enzyme which is required to produce the amino acids valine, leucine, and isoleucine in plants. Because these amino acids are not produced by humans or animals, these compounds are relatively low in acute and chronic toxicity. Additional favorable characteristics of these compounds include an unusually broad spectrum of crop selectivity, weed control efficacy, and a favorable environmental profile (Moberg and Cross 1990). Degradation products of trifloxysulfuron are not herbicidally active. The water solubility of this herbicide is influenced by pH as well as the chemical hydrolysis (Hudetz et al. 2000).

Trifloxysulfuron has activity on numerous broadleaf, grass, and sedge species (Koger et al. 2005; Porterfield et al. 2003; Richardson et al. 2004) that are troublesome in row crop production systems. Porterfield et al. (2002) found that trifloxysulfuron provided at least 70% control of common ragweed (*Ambrosia artemisiifolia* L.), entireleaf morningglory (*Ipomoea hederacea* var. *integriuscula* Gray), pitted morningglory, sicklepod, tall morningglory [*Ipomoea purpurea* (L.) Roth], and yellow nutsedge. Another study found that trifloxysulfuron applied POST provided excellent control of sicklepod, Palmer amaranth, and hemp sesbania (*Sesbania herbacea* (P. Mill.)

McVaugh) (Branson et al. 2005). Burke and Wilcut (2004) reported that trifloxysulfuron controlled common lambsquarter, common ragweed, Palmer amaranth (*Amaranthus palmeri* L.), sicklepod, smooth pigweed (*Amaranthus hybridus* L.), and morningglory species.

A review of the literature yields little information on spray solution stability. Whisenant and Bovey (1993) found that water quality affected the phytotoxicity of picloram on honey mesquite (*Prosopis glandulosa* Torr.) when mixtures were sprayed 168 h after mixing. SUs hydrolyze more rapidly in water at acidic pH compared to neutral solutions (Sarmah and Sabadie 2002). Vicari et al. 1996 found that rimsulfuron hydrolysis in aqueous solution decreased with increasing pH up to pH 7, then increased again under alkaline conditions. However, weak acid herbicides, such as trifloxysulfuron, exist to a greater extent in the neutral form at pH values near  $pK_a$ . The undissociated acid diffuses across the plasma membrane more easily than the dissociated, charged particle (Sterling 1994). This suggests that acidic pH would enhance herbicide absorption. Previous research has shown lower absorption and translocation of trifloxysulfuron compared to other SUs in weeds that are typically difficult to control (McElroy et al. 2004). Perhaps these differences can be attributed to pH of the spray solution. SU herbicides are usually formulated as dry material. To achieve maximum activity, the dry particles must be solubilized in the spray mixture, spray deposit, or within the plant (Green and Cahill 2003). Water solubility values of SUs change dramatically in response to changes in pH (Vencill 2002). The water solubility limit of trifloxysulfuron is  $63 \text{ mg L}^{-1}$  at pH 5 and  $5016 \text{ mg L}^{-1}$  at pH 7 (Hudetz

et al. 2000). DuPont researchers have indicated that the addition of adjuvants that increase pH of the spray mixture has increased the biological activity of another SU, nicosulfuron (Green and Cahill 2003). The water quality used for spray applications can vary significantly depending upon the source.

Palmer amaranth and Texasweed (*Caperonia palustris* (L.) St. Hil.) are annual broadleaf weeds that are troublesome in Texas cotton production. Morgan et al. (2001) reported that cotton yields decreased linearly from 13 to 54% as a result of 1 to 10 Palmer amaranth plants per 9.1 m of row. Furthermore, Palmer amaranth in cotton can also affect mechanical harvest time. Densities of 650, 1,300, and 3,260/ha Palmer amaranth plants significantly increased cotton harvest time compared with the weed-free check (Smith et al. 2000). In recent years, Texasweed has become a problem in cotton grown along the Texas Upper Gulf Coast. Texasweed seed is capable of germinating and surviving under a broad range of climatic and edaphic conditions (Koger et al. 2004). It is difficult to control with glyphosate and other cotton herbicides. Matocha and Baumann (2004) reported poor control of Texasweed from pyriithiobac, MSMA, DSMA, and fluometuron when plant height was  $\geq 15$  cm.

Trifloxysulfuron has an ionizable functional group with a  $pK_a$  of 4.81. At neutral pH the octanol-water partition coefficient ( $K_{ow}$ ) for trifloxysulfuron is 0.37, and its water solubility is 5016 mg L<sup>-1</sup> (Hudetz 2000). Consequently, trifloxysulfuron will be in the anionic form at near-neutral soil pH and should partition predominately into the aqueous phase. However, sorption data for trifloxysulfuron have not been published. The sorption of trifloxysulfuron to soil will likely be similar to that of other SUs. Freundlich

sorption coefficients ( $K_f$ ) for rimsulfuron, chlorosulfuron, imazosulfuron, metsulfuron-methyl, azimisulfuron, and triasulfuron range from 0.23 to 6.34 (Berglof et al. 2003; Mersie and Foy 1986; Morrica et al. 2000; Pusino et al. 2003; Pusino et al. 2004; Reddy et al. 1995; Reddy and Locke 1998; Schneiders et al. 1993). Generally, sorption of SUs in soil is low, negatively correlated with pH, and positively correlated with soil organic carbon. Since sorption is inversely correlated with mobility, SUs are potentially mobile in soil.

The potential for off-site transport of SUs has been documented in surface water monitoring studies, natural rainfall and simulated rainfall studies. In a large scale monitoring study conducted in the Midwestern United States, 212 water samples were collected from 75 surface-water sites and 25 ground water sites (Battaglin et al. 2000). At least one of the 16 targeted SUs was detected above the method reporting limit of  $0.01 \text{ ug L}^{-1}$  in 83% of the stream samples, 86% of the reservoir samples, and 24% of the ground water samples. In a natural rainfall study, fractional losses of sulfosulfuron applied post-emergence to winter wheat at  $19.8 \text{ g a.i. ha}^{-1}$  were 0.5% (Brown et al. 2004). In a simulated rainfall study, fractional losses of chlorimuron ethyl and nicosulfuron applied post-emergence at  $14 \text{ g a.i. ha}^{-1}$  to soybean and corn, respectively, did not exceed 2.2% (Afyuni et al. 1997). Fractional losses of sulfometuron-methyl applied at  $0.4 \text{ kg ha}^{-1}$  as either a dispersible granule or an emulsifiable concentrate to a mixed stand of common bermudagrass/bahiagrass and bare plots did not exceed 2% for any treatment (Wauchope et al. 1990).

The objectives of this research were to quantify the dissipation of trifloxysulfuron in a spray tank at 0, 1, 3, 7, 14, and 21 d after mixing as influenced by pH of the spray carrier and evaluate the resulting effects on efficacy on Palmer amaranth; to determine the effect of spray carrier pH on absorption and translocation of radiolabeled trifloxysulfuron in Palmer amaranth and Texasweed; and to determine average edge-of-field concentrations, total mass losses, and fractional losses of trifloxysulfuron applied to cotton at the 5-leaf stage and to bare soil as influenced by simulated rainfall.



**CHAPTER II**  
**TRIFLOXYSULFURON DISSIPATION AT SELECTED pH LEVELS AND**  
**EFFICACY ON PALMER AMARANTH (*Amaranthus palmeri* S. Wats)**

**Introduction**

Due to their chemical properties, the SU herbicides have the potential to chemically degrade in aqueous solution. The most common degradation pathways for SUs include chemical hydrolysis and microbial degradation (Sarmah et al. 2000). SUs have many functional groups susceptible to different hydrolysis reactions. The main chemical degradation reaction is the pH-dependent cleavage of the sulfonylurea bridge (Berger and Wolfe 1996). In addition to the potential for chemical hydrolysis, the water solubility of SUs is also dependent upon pH. In general, SU water solubility decreases with pH.

Herbicides must be solubilized in spray solution before they are applied in order to be absorbed by leaves of weeds. When spray carrier pH levels are low, SUs form dispersions preventing the active ingredient from solubilizing and, therefore, reduce effectiveness (Green and Cahill 2003). Pesticide applicators can not always apply pesticides immediately after mixing. Numerous factors such as distance from mixing/loading sites to application sites, spray tank size, and weather conditions may affect the time interval between herbicide mixing and application. The greater the time interval, the greater the potential for herbicide deactivation.

Trifloxysulfuron is an SU herbicide labeled for application in cotton, turf, and sugarcane. The effects of reduced solubility on this compound as a result of pH are unknown. Likewise, the rate of chemical degradation over time in the spray tank as influenced by pH is also unknown for this compound. Previous research has shown that SUs hydrolyze more rapidly in water at acidic solution pH values, but remain relatively stable in neutral or alkaline solutions (Sarmah and Sabadie 2002). Data providing information on pH influence on chemical hydrolysis and effectiveness of trifloxysulfuron would be helpful to pesticide applicators. Therefore, the objectives of this work were to determine the effect of spray carrier pH on dissipation of trifloxysulfuron in the spray tank during a 21 d period and to evaluate the resulting effects on efficacy on Palmer amaranth.

## **Materials and Methods**

### **Trifloxysulfuron dissipation**

Treatment solutions were prepared to simulate a spray tank dissipation scenario. Deionized water was used to prepare buffer solutions at pH levels of 5, 7, and 9. Buffer solutions were prepared by using varying combinations of 0.1M NaOH and 0.1M  $\text{KH}_2\text{PO}_4$ . Final pH was measured using a pH meter<sup>1</sup>. Glass scintillation vials were filled with 20 ml of buffer solutions and formulated trifloxysulfuron and non-ionic surfactant<sup>2</sup> (NIS) was added to each vial to give rates of 5.25 g a.i. ha<sup>-1</sup> and 0.25% v/v, respectively. Treatments consisted of pH 5, 7, and 9 prepared at 0, 1, 3, 7, 14, and 21 d before being quantified. Each treatment was replicated three times and the experiment was repeated.

Spray solutions were stored in a growth chamber at 22( $\pm$ 2) C and covered with aluminum foil to limit photolysis prior to application.

Trifloxysulfuron remaining in solution was quantified using high performance liquid chromatography (HPLC). A 250- $\mu$ l aliquot was removed from each treatment and combined with 750  $\mu$ l of acetonitrile. All solvents were HPLC-grade and consisted of acetonitrile and 0.30 mM dibasic potassium phosphate buffer at pH 2.7 (4/6,v/v). Buffered mobile phase was adjusted to pH 2.7 with 85% aqueous phosphoric acid. Mobile phase flow rate was constant at 0.8 mL min<sup>-1</sup>. A 10- $\mu$ l sample was injected into HPLC mobile phase and passed through a Symmetry<sup>®</sup> C-18 column held at 20 C. A Waters 996 Photodiode Array was used for detection. Retention time for trifloxysulfuron was 4.0 min. A chromatogram of a trifloxysulfuron standard is shown in Figure 1 and the absorbance spectra in Figure 2. Half-life values were calculated for each pH level using linear regression of first-order equations of each pH treatment.

## Bioassay

Palmer amaranth seeds were planted directly into 11-cm (i.d.) pots containing a mixture of Weswood silt loam and potting soil (1:1, v/v). Upon emergence, plants were thinned to two plants per pot. Plants were grown outdoors for the entire duration to simulate field environmental conditions and were subirrigated as needed.

Trifloxysulfuron buffer solutions were prepared as previously described at 0, 1, 3, 7, and 14 d before treatment (DBT) and were applied to actively growing Palmer amaranth plants in the 6- to 8-leaf stage to evaluate efficacy effects of pH and dissipation.

Treatments were applied using a moving-boom spray chamber equipped with a 8004E flat-fan nozzle utilizing compressed air delivering 187 L ha<sup>-1</sup> operating at 241 kPa.

Aerial plant portions of Palmer amaranth were harvested 14 d after treatment, oven dried at 45 C, and dry weights recorded. Each treatment was replicated three times and the experiment was repeated. Plant dry weights were converted into percent reduction based on the untreated and means were separated using Fisher's protected least significant difference at  $P < 0.05$ . Arcsine transformation of percentages did not affect the results; therefore, untransformed data were used in the analysis.

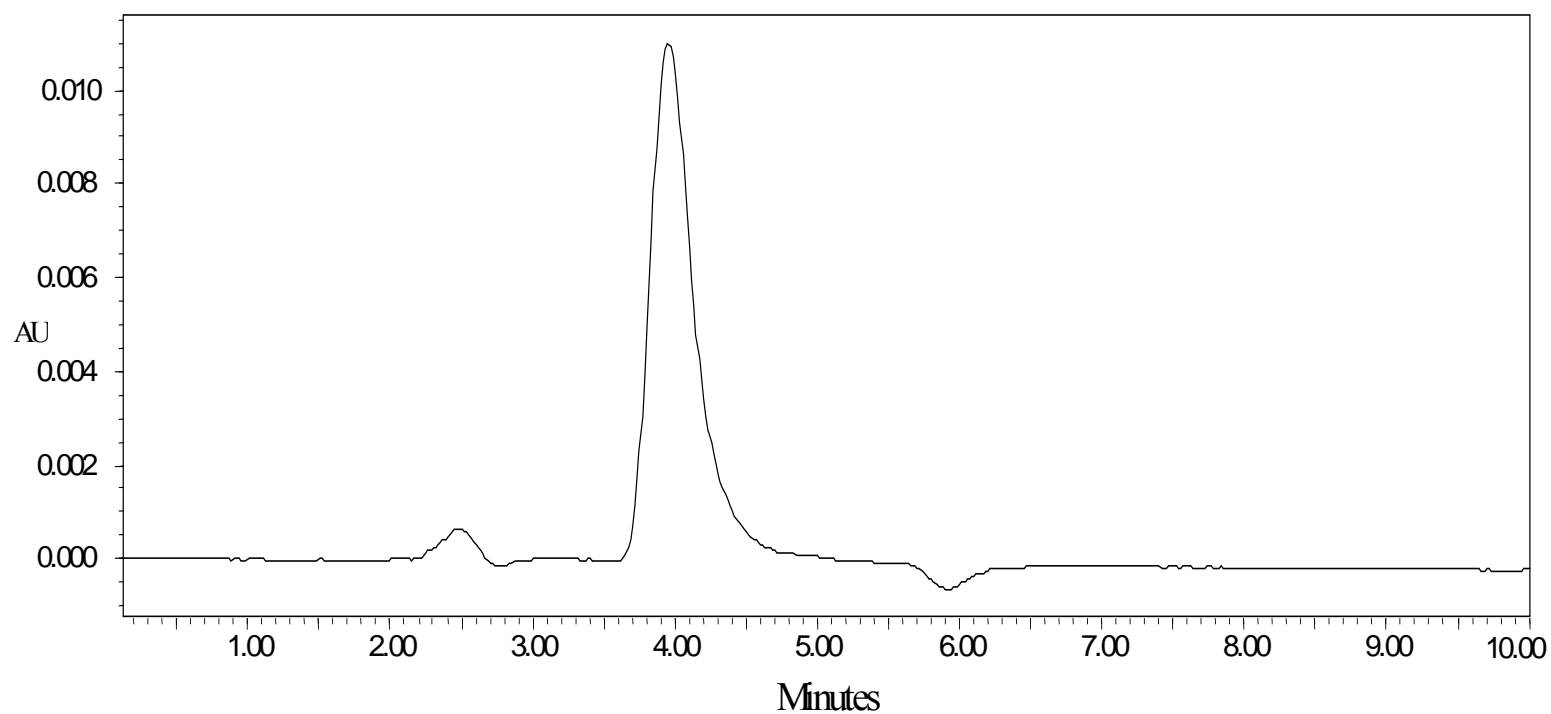


Figure 1. Chromatogram of a  $10\text{ }\mu\text{g ml}^{-1}$  standard of trifloxysulfuron at 245-nm extracted from data collected by a photodiode array. The y-axis represents absorbance units (AU) and the x-axis represents retention time.

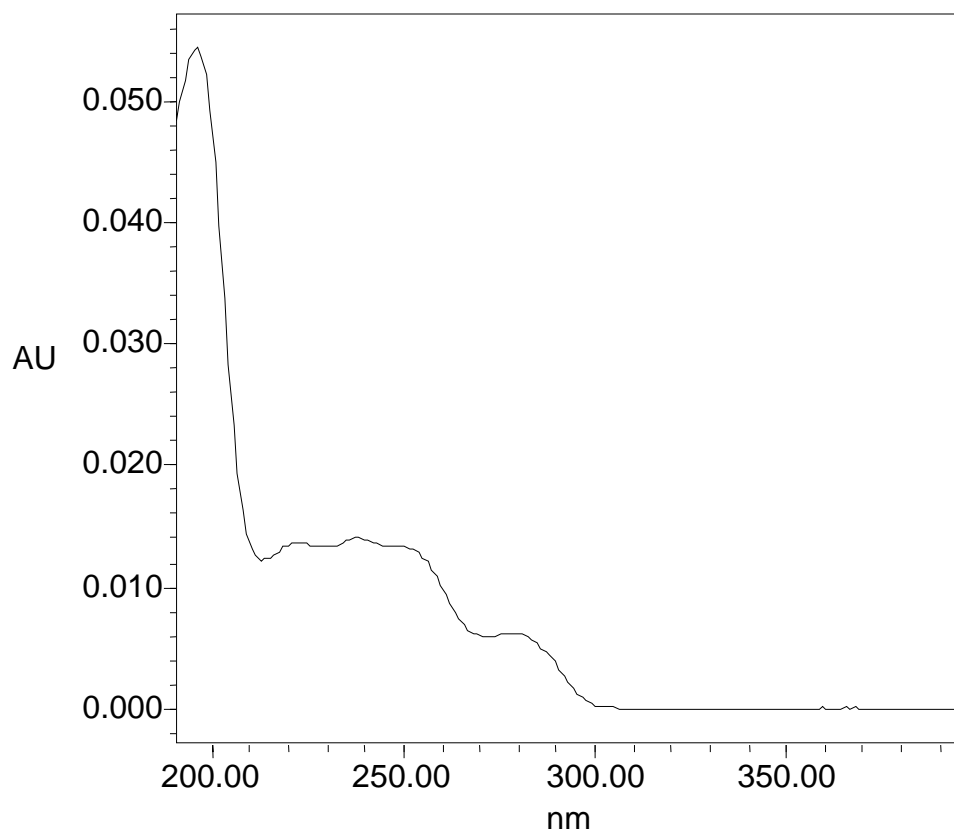


Figure 2. Absorbance spectra of trifloxysulfuron extracted from a  $10 \mu\text{g ml}^{-1}$  standard using a photodiode array detector.

## Results and Discussion

### Trifloxysulfuron dissipation

The dissipation of trifloxysulfuron followed first-order kinetics. The first-order rate constant, the half-lives, and correlation coefficients are shown in Table 1. First-order kinetic plots for each spray solution pH were constructed (Figure 3). Calculated half-life values indicate that hydrolysis occurs most rapidly under acidic spray carrier pH with little or no difference between neutral and alkaline pH levels. More rapid hydrolysis of SUs under acidic conditions has been reported for bensulfuron-methyl, sulfometuron-methyl, tribenuron-methyl, nicosulfuron, chlorimuron-ethyl, thifensulfuron-methyl, metsulfuron-methyl, chlorsulfuron, and amidosulfuron (Berger and Wolfe 1996). Likewise, rapid hydrolysis at acidic pH has been reported for triasulfuron, sulfosulfuron, prosulfuron, primisulfuron, imazosulfuron, triflusulfuron, and trifloxysulfuron in aqueous solutions (Braschi et al. 1997; Braschi et al. 2000;

Hudetz et al. 2000; Hultgren et al. 2002; Morrica et al. 2001; Saha and Kulshrestha 2002; Vega et al. 2000).

The half-life value for pH 5 of 12.8 d is significantly greater than the reported  $DT_{50}$  value in water/buffer solution of 6 d (Hudetz et al. 2000). The most likely explanation for the difference in dissipation values is the temperature differential between the two studies. The temperature for buffer solutions in this study was 22 C while the temperature for the previous study was 25 C (Hudetz et al. 2000). It has been reported that the rate of chemical degradation of SUs increases with increasing temperature (Braschi et al. 2000). The difference in dissipation values may also be due to differences in herbicide material. In this study, formulated trifloxysulfuron was used while it is possible that the previous study used technical grade herbicide. Differences in formulation materials may account for longer half-life values found in this study. Also, NIS was mixed with formulated herbicide in this study and may have affected hydrolysis.



Table 1. First-order rate constant (k), half-life ( $t_{1/2}$ ), and coefficient of determination ( $R^2$ ) for trifloxysulfuron dissipation in deionized water adjusted to pH values of 5, 7, and 9.

pH	Rate constant	$t_{1/2}$	Coefficient of determination
	k	d	$R^2$
5	-0.054	13	0.99
7	-0.019	36	0.97
9	-0.020	35	0.92

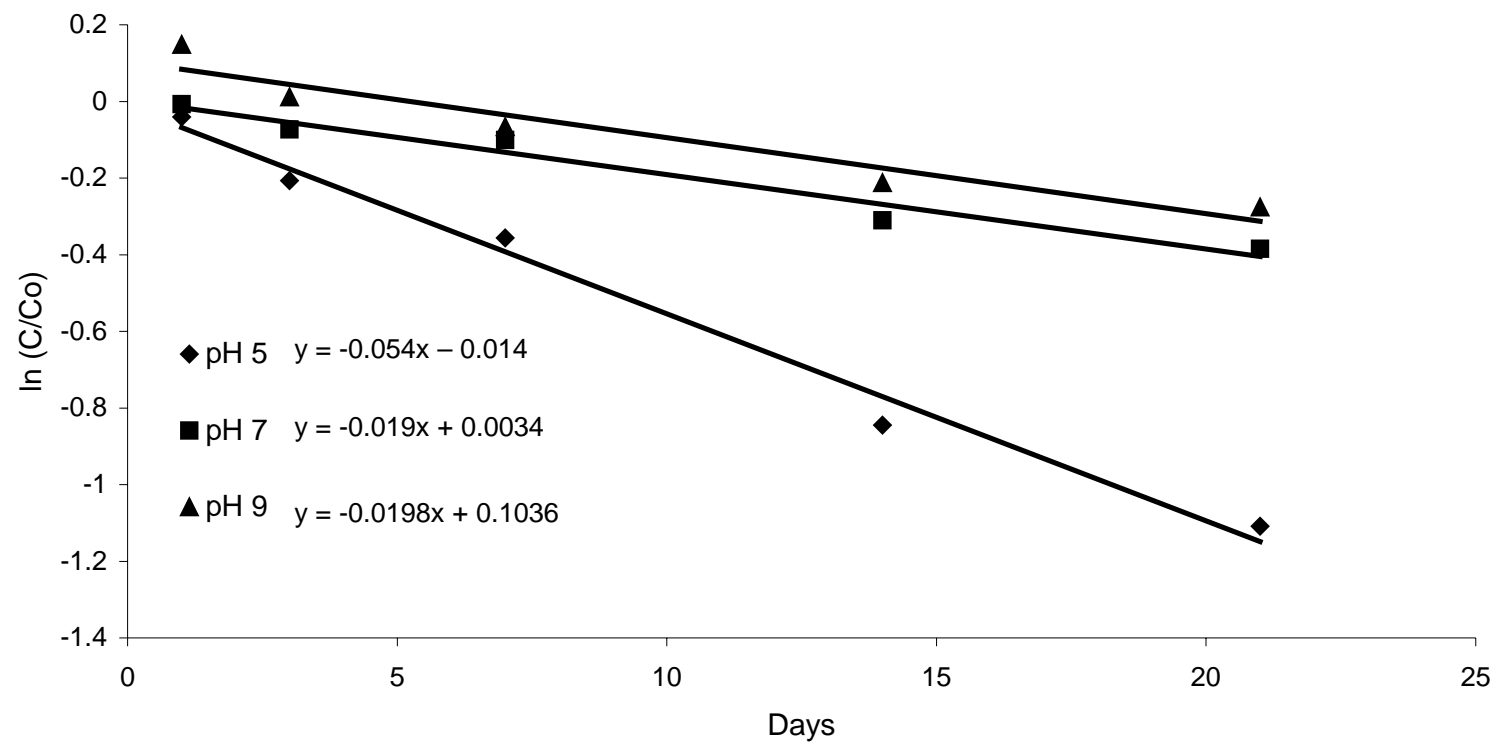


Figure 3. First-order rate plots for dissipation of trifloxysulfuron in deionized water adjusted to pH values of 5, 7, and 9.

**Bioassay**

Palmer amaranth plants treated with trifloxysulfuron buffer solutions showed significant growth reduction compared to untreated plants (Table 2). At all pH levels and time intervals solutions were prepared prior to application, trifloxysulfuron solutions significantly decreased dry weights compared to untreated.

When dry weights are expressed as a percent reduction based on untreated, Palmer amaranth plants treated with pH 5 solution showed significantly less reduction in dry weights when solution was prepared 14 DBT compared to 0 or 1 DBT (Table 2). No differences were observed in plants treated with pH 7 or pH 9 solutions. Although these changes in dry weights are small compared to the untreated, the data indicate decreasing efficacy of trifloxysulfuron at the acidic pH level over time.

Dry weight reduction at all pH levels and time intervals compared to the untreated indicate that Palmer amaranth is more susceptible to trifloxysulfuron than previously anticipated. Dissipation data indicates that at least 50% of trifloxysulfuron dissipated from pH 5 solution by 13 d after preparation of the solution. Correlation between bioassay and dissipation data show positive correlations for acidic and neutral pH levels and a lack of correlation at the alkaline pH (Table 3.). Although small increases in dry weights over time were observed, bioassay data suggests that trifloxysulfuron efficacy on Palmer amaranth is significant at 50% of the labeled rate. Moreover, it is possible that the more rapid dissipation at pH 5 was offset by increased absorption at acidic pH due to greater proportion of herbicide molecules being present in the undissociated form.

Table 2. Percent reduction based on untreated tissue of Palmer amaranth dry weights treated with trifloxysulfuron spray carrier solutions at pH levels 5, 7, and 9 prepared 0, 1, 3, 7, and 14 d prior to application<sup>a</sup>.

Days	pH level		
	5	7	9
	%		
0	94.4	97.1	95
1	96.3	97.6	95.4
3	92.1	95	94.8
7	92.4	95.5	96.1
14	89.7	93.3	95.5
LSD (0.05)	3.1	NS	NS

<sup>a</sup> Trifloxsulfuron rate was 5.25 g a.i. ha<sup>-1</sup>.

Table 3. Correlation coefficients between percent dry weight reduction vs. percent remaining in solution at various incubation times.

pH level	Correlation coefficient
5	.913
7	.908
9	-.282

**CHAPTER III**

**EFFECT OF SPRAY CARRIER pH ON ABSORPTION AND  
TRANSLOCATION OF TRIFLOXYSULFURON IN PALMER AMARANTH  
(*Amaranthus palmeri* S. Wats) AND TEXASWEED (*Caperonia palustris* (L.) St.  
Hil.)**

**Introduction**

Trifloxysulfuron is a sulfonylurea (SU) herbicide developed for postemergence weed control in cotton (*Gossypium hirsutum* L.), sugarcane (*Saccharum* spp.) and turfgrass (Holloway et al. 2000; Hudetz et al. 2000). It is a weak acid with a  $pK_a$  of 4.81, and its water solubility is related to the  $pK_a$  of the hydrogen atom on the sulfonylurea bridge and the pH of the solution. The water solubility of trifloxysulfuron at pH 5 and 7 is 63 mg L<sup>-1</sup> and 5016 mg L<sup>-1</sup>, respectively (Vencill 2002). Despite the pH dependency of SUs, few studies have evaluated the effect of carrier pH on the absorption and translocation of SUs and specifically trifloxysulfuron when applied to foliage of susceptible plants.

Generally, the uptake of weak acids by plant tissues is greater at lower carrier pH due to a higher proportion of the molecules being present in an undissociated form. Yet, Liu et al. (2002) reported greater uptake of bentazon by white mustard (*Sinapsis alba* L.) and wheat (*Triticum aestivum* L.) leaves at pH 7 and 9 compared to pH 5. Absorption of bentazon by bean (*Vicia faba* L.) was minimal regardless of carrier pH. Similarly, researchers have indicated that the addition of adjuvants that increased pH of the spray mixture increased the biological activity of nicosulfuron in low carrier volume on

difficult to control weeds (Green and Cahill 2003). Collectively, these studies indicate that increasing the pH of the carrier solution may enhance absorption and translocation of trifloxysulfuron in some species.

Trifloxysulfuron has activity on numerous broadleaf, grass, and sedge species (Koger et al. 2005; Porterfield et al. 2003; Richardson et al. 2004) that are troublesome in row crop production systems. Trifloxysulfuron has activity on several broadleaf species such as pitted morningglory, hemp sesbania, and velvetleaf (*Abutilon theophrasti* Medik.).

Palmer amaranth and Texasweed are annual broadleaf weeds that are troublesome in cotton production. Morgan et al. (2001) reported that cotton yields decreased linearly from 13 to 54% as a result of 1 to 10 Palmer amaranth plants per 9.1 m of row. Moreover, Palmer amaranth in cotton can reduce mechanical harvest time at densities greater than 650 plants ha<sup>-1</sup> (Smith et al. 2000). In recent years, Texasweed has become a problem weed in soybean and rice production in the midsouth USA (Koger et al. 2004) and in cotton along the Texas Upper Gulf Coast (Matocha and Baumann 2004). Texasweed seed germinates and survives under a broad range of climatic and edaphic conditions (Koger et al. 2004) and is difficult to control with glyphosate and other cotton herbicides including pyriithiobac, MSMA, DSMA, and fluometuron (Matocha and Baumann 2004). Adjusting the pH of the spray carrier may enhance absorption and translocation of trifloxysulfuron by these species. Therefore, studies were conducted to evaluate the absorption and translocation of foliar-applied trifloxysulfuron in Palmer amaranth and Texasweed as influenced by pH of the spray carrier.

## **Materials and Methods**

### **Plant material**

Palmer amaranth and Texasweed plants were propagated from seed in a greenhouse. Texasweed seeds were planted in 26- by 52- by 6-cm trays containing a mixture of Bosket sandy loam (fine-loamy, mixed thermic Mollic Hapludalfs) and Jiffy Mix potting soil<sup>1</sup> (1:1, v/v). Seeds were spread on top of the soil mixture and subirrigated with distilled water. After emergence, seedlings in the cotyledon growth stage were transplanted into 11-cm-diam. pots containing Jiffy Mix potting soil. Palmer amaranth seeds were planted directly into 11-cm-diam. pots containing a mixture of Bosket sandy loam and Jiffy Mix potting soil (1:1, v/v). Each treatment unit consisted of 1 plant per pot. Plants were grown at 32/25 C ( $\pm$  3 C) day/night temperature and were subirrigated as needed. Palmer amaranth plants were at the 6- to 8-leaf stage and Texasweed plants were at the 3- to 4-leaf stage when <sup>14</sup>C-trifloxysulfuron was applied. Plants were not presprayed with formulated trifloxysulfuron before application of <sup>14</sup>C-trifloxysulfuron to minimize stress during the exposure period. Pretreated (Camacho and Moshier 1991) and nontreated (Gillespie 1994) plants have produced similar absorption and translocation trends when leaves were spot treated with sulfonylurea herbicides.

### **Absorption and translocation**

Technical grade [pyridinyl-2-<sup>14</sup>C] trifloxysulfuron with 815.7 kBq  $\mu$ mol<sup>-1</sup> specific activity and 95.9% radiochemical purity was used in these experiments. <sup>14</sup>C-trifloxysulfuron was dissolved in HPLC-grade methanol and deionized water.



Radioactive solutions were a mixture of  $\text{KH}_2\text{PO}_4$ :NaOH buffered deionized water at pH 5, 7, or 9 and 0.25% v/v NIS<sup>2</sup>. The final treatment solution contained 5% (v/v) methanol. A 5- $\mu\text{l}$  volume of each treatment solution containing 2.8 kBq radioactivity was placed as 15 droplets using a micro-syringe on the adaxial surface of the fourth true leaf of Palmer amaranth or the second true leaf of Texasweed.

Plants were harvested at 4, 24, 48, and 72 h after treatment (HAT) and separated into treated leaf, aerial sections above and below treated leaf, and roots. The treated leaf, including the petiole, was rinsed by gently shaking for 15 s with 15 ml methanol:water (1:1, v/v) to remove nonabsorbed herbicide. Two 1-ml aliquots of the leaf rinse were added to 10 ml of scintillation fluid (EcoLume<sup>3</sup>), and radioactivity was quantified via liquid scintillation spectrometry<sup>4</sup> (LSS). Plant sections were wrapped in tissue paper<sup>5</sup>, placed in glass scintillation vials and oven dried for 48 h at 45 C. Oven-dried plant samples were combusted with a biological sample oxidizer<sup>6</sup>. Sample radioactivity was quantified by LSS.

The amount of  $^{14}\text{C}$  present in the leaf washes and plant sections was considered as total  $^{14}\text{C}$  recovered, which averaged 91% of applied  $^{14}\text{C}$ -trifloxysulfuron. The sum of the radioactivity present in all plant parts was considered as absorption and expressed as percentage of the  $^{14}\text{C}$  recovered. Radioactivity in all plant parts except the treated leaf was considered as translocated and expressed as a percentage of the  $^{14}\text{C}$  recovered.

Treatments were replicated three times and the experiment was repeated. Data were subjected to analysis of variance (ANOVA) with sums of squares partitioned to reflect a split-split-plot treatment structure and trial effects. The four harvest timings

were considered as main plots, the two species were considered subplots, and the three pH levels were considered sub-subplots. Trial effects were considered random, and mean squares were tested appropriately based on the treatment design (McIntosh 1983). Where main plot effects were significant, regressions were used to explain the relationship of measured responses over time. Where appropriate, significant main effects were averaged over harvest interval, species, and/or pH and separated by Fisher's protected least significant difference at  $P < 0.05$ .

## Results and Discussion

Trial effects were not significant at any harvest interval, plant species, or pH. Statistical significance levels for absorption, translocation, and partitioning to selected plant sections of trifloxysulfuron are shown in Table 4. Main effects for the absorption of  $^{14}\text{C}$ -trifloxysulfuron were significant. Main effect of harvest interval was pooled over species and pH, while species main effect was pooled over harvest interval and pH. Main effect of pH was pooled over harvest interval and species.

Absorption of  $^{14}\text{C}$ -trifloxysulfuron followed a logarithmic trend with the majority of the herbicide absorbed by 24 HAT (Figure 4). A logarithmic increase in the foliar absorption of trifloxysulfuron has been reported for various species including cotton, jimsonweed (*Datura stramonium* L.), peanut (*Arachis hypogaea* L.), sicklepod [*Senna obtusifolia* (L.) Irwin and Barneby], purple nutsedge (*Cyperus rotundus* L.), yellow nutsedge (*Cyperus esculentus* L.), green kyllinga (*Kyllinga brevifolia* Rottb.), and false green kyllinga (*Kyllinga gracillima* L.) (Askew and Wilcut 2002; McElroy et al. 2004;

Table 4. Statistical significance levels for absorption, translocation, and partitioning to selected plant sections of trifloxysulfuron in Palmer amaranth and Texasweed at pH levels 5, 7, and 9<sup>a</sup>.

Effect	df <sup>b</sup>	P > F					
		Absorption	Translocation	Treated Leaf	Above Treated Leaf	Below Treated Leaf	Roots
Block	5	0.5822	0.4089	0.4457	0.7757	0.0944	0.1014
Time	3	<0.0001*	<0.0001*	<0.0001*	<0.0001*	<0.0001*	0.0006*
Species	1	<0.0001*	<0.0001*	<0.0001*	<0.0001*	<0.0001*	0.2753
pH	2	0.0011*	0.0189*	0.0041*	0.3958	0.0197*	0.0468*
Time * Species	3	0.1855	0.0132*	0.4520	0.0024*	0.1072	0.0872
Time * pH	6	0.2188	0.0754	0.1360	0.2888	0.0705	0.0306*
Species * pH	2	0.5308	0.0222*	0.9269	0.2786	0.0516	0.0168*
Time * Species * pH	6	0.2204	0.0094*	0.6701	0.0959	0.1913	0.0711

<sup>a</sup> \* Factors were significant at the 0.05 level of probability.

<sup>b</sup> Degrees of freedom were the same for all parameters.

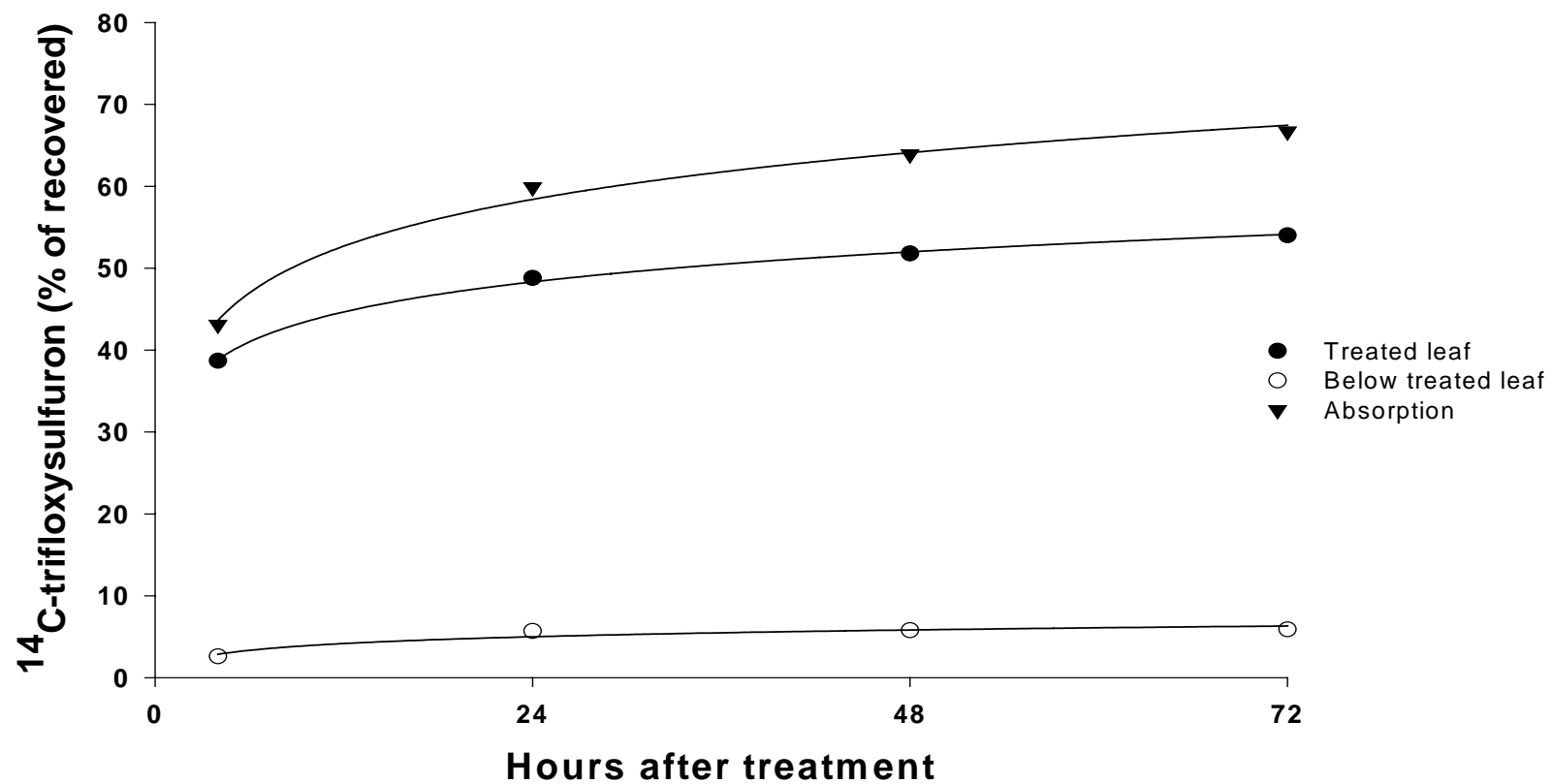


Figure 4. Absorption and accumulation of  $^{14}\text{C}$ -trifloxysulfuron in treated leaves and below treated leaf plant sections averaged over three spray carrier pH values (5, 7, and 9) and plant species (Palmer amaranth and Texasweed).

Troxler et al. 2003). Generally, for the aforementioned studies, absorption of trifloxysulfuron was rapid and occurred by 4 HAT.

Absorption of  $^{14}\text{C}$ -trifloxysulfuron by Palmer amaranth was greater than that by Texasweed (Table 5). Differential absorption among species has been reported previously. Askew and Wilcut (2002) reported that absorption of  $^{14}\text{C}$ -trifloxysulfuron decreased in the order of jimsonweed > sicklepod > peanut > cotton. Wilcut et al. (2000) reported > 95% early season control of Palmer amaranth with trifloxysulfuron. Low absorption of  $^{14}\text{C}$ -trifloxysulfuron by Texasweed may contribute to poor weed control observed along Texas Upper Gulf Coast (Paul Baumann, personal communication).

Absorption of trifloxysulfuron decreased in the order of pH 9 = pH 7 > pH 5 (Table 6). Greater absorption of trifloxysulfuron at high pH is in contrast to most weak acid herbicides. Liu (2002) noted that the absorption of most weak acid herbicides into plant tissues is greater at a low carrier pH due to a greater proportion of the molecules being present in an undissociated form. However, most of the reviewed studies were conducted with plant tissues immersed or cultured cells incubated in a solution of non-formulated weak acid herbicides (Liu 2002). To our knowledge, no study has reported on the effect of carrier pH on the absorption of sulfonylurea herbicides into plant foliage *in vivo*. However, Liu (2002) observed greater absorption of bentazon by white mustard and wheat with spray carrier pH of 7 and 9 as compared to pH 5. Another study found that the addition of adjuvants that increased pH of the spray mixture increased the biological activity of high nicosulfuron rates at low spray volumes on difficult-to-control

Table 5. Absorption and distribution of  $^{14}\text{C}$ -trifloxysulfuron into treated leaves and below treated leaf plant sections in Palmer amaranth and Texasweed averaged over time and pH (5, 7, and 9).<sup>a</sup>

Species	Absorption <sup>b</sup>	$^{14}\text{C}$ -trifloxysulfuron distribution <sup>c</sup>	
		Treated leaf	Below treated leaf
		----- % of recovered -----	
Palmer amaranth	88.0	73.7	7.1
Texasweed	28.8	23.0	2.9
LSD (0.05)	1.2	3.3	0.8

<sup>a</sup> Plants were maintained in the greenhouse at 32/25 C day/night temperature.

<sup>b</sup>  $^{14}\text{C}$  present in all plant parts was considered as absorption and expressed as percentage of the  $^{14}\text{C}$  recovered.

<sup>c</sup>  $^{14}\text{C}$ -trifloxysulfuron distribution throughout the plant is based on percent of  $^{14}\text{C}$ -trifloxysulfuron recovered.

Table 6. Effect of pH (5, 7, and 9) on absorption and partitioning of  $^{14}\text{C}$ -trifloxysulfuron to treated leaves and below treated leaf plant sections averaged over time and plant species.<sup>a</sup>

pH	Absorption <sup>b</sup>	$^{14}\text{C}$ -trifloxysulfuron distribution <sup>c</sup>	
		Treated leaf	Below treated leaf
	-----	% of recovered	-----
5	53.8	44.9	4.4
7	60.4	50.1	5.5
9	61.0	50.0	5.2
LSD (0.05)	1.4	3.5	0.8

<sup>a</sup> Plants were maintained in the greenhouse at 32/25 C day/night temperature.

<sup>b</sup>  $^{14}\text{C}$  present in all plant parts was considered as absorption and expressed as percentage of the  $^{14}\text{C}$  recovered.

<sup>c</sup>  $^{14}\text{C}$ -trifloxysulfuron distribution throughout the plant is based on percent of  $^{14}\text{C}$ -trifloxysulfuron recovered.

weeds (Green and Cahill 2003).

Decreased absorption of trifloxysulfuron at pH 5 may be due to reduced solubility at low solution pH values. Liu (2002) noted that solubility in droplet residue can affect the uptake of weakly acidic molecules, perhaps by crystallization on the leaf surface. At pH 7 and 9, spray carriers produce more dissociated anions that encounter greater difficulty in diffusing through the non-polar plant cuticle and, therefore, this effect may be offset by greater water solubility of trifloxysulfuron at higher solution pH values.

The main effects and interaction of pH, species, and harvest intervals were significant ( $P < 0.05$ ) for the translocation of trifloxysulfuron. Therefore, translocation data were analyzed by weed species. Altering pH did not affect the translocation of trifloxysulfuron in Palmer amaranth (Table 7). In contrast, translocation of  $^{14}\text{C}$ -trifloxysulfuron in Texasweed at 72 HAT increased in the order of pH 5 (5%) < pH 7 (10%) = pH 9 (10%). Translocation from 4 to 72 HAT was significant in both species except in Texasweed at pH 5, which was likely a function of reduced absorption. Less than 11 and 20% of recovered  $^{14}\text{C}$ -trifloxysulfuron moved out of the treated leaves of Texasweed and Palmer amaranth, respectively. Wilcut et al. (1989) found that although two crop species and four weed species varied in amounts of  $^{14}\text{C}$ -chlorimuron that moved out of the treated leaf, no species translocated > 25% of the applied radioactivity.

For recovery of  $^{14}\text{C}$ -trifloxysulfuron in the treated leaf and below treated leaf, main effects for harvest interval, species, and pH were significant. Averaged over species and pH, the recovery of trifloxysulfuron increased logarithmically for both



Table 7. Translocation of  $^{14}\text{C}$ -trifloxysulfuron in Palmer amaranth and Texasweed as related to spray carrier pH and harvest interval.<sup>a</sup>

Species	pH	Harvest interval				LSD
		4	24	48	72	
		----- % of recovered -----				
Palmer amaranth	5	7.8 <sup>b</sup>	13.9	18.7	16.6	4.4
	7	6.3	14.7	18.5	18.1	5.1
	9	5.8	19.4	14.9	16.3	3.4
LSD		NS	NS	NS	NS	
Texasweed	5	2.4	3.0	4.7	4.6	NS
	7	1.7	10.2	7.0	10.4	4.2
	9	2.1	5.5	9.0	10.1	4.5
LSD		NS	3.6	NS	5.1	

<sup>a</sup> Plants were maintained in the greenhouse at 32/25 C day/night temperature.

<sup>b</sup> LSD may be used for comparison of mean values within species.

treated leaf and below treated leaf (Figure 4). Previous research also showed logarithmic trends for  $^{14}\text{C}$ -trifloxysulfuron recovered from plant parts (Troxler et al. 2003). Averaged over time and pH, the recovery of trifloxysulfuron was greater in the treated leaf and below treated leaf for Palmer amaranth compared to Texasweed (Table 5). Another study found that jimsonweed absorbed and translocated more  $^{14}\text{C}$ -trifloxysulfuron than other weed and crop species (Askew and Wilcut 2002). However, the majority of recovered  $^{14}\text{C}$ -trifloxysulfuron remained in the treated leaf. Troxler et al. (2003) also reported that the majority of applied  $^{14}\text{C}$ -trifloxysulfuron remained in treated leaves of yellow and purple nutsedge. Less than 6% of  $^{14}\text{C}$ -nicosulfuron and primisulfuron moved out of treated leaves of eastern black nightshade (*Solanum ptycanthum* Dun.) (Carey et al. 1997). Averaged over species and harvest interval, recovery of  $^{14}\text{C}$ -trifloxysulfuron increased in the order of  $\text{pH } 5 < \text{pH } 7 = \text{pH } 9$ . Greater translocation of  $^{14}\text{C}$ -trifloxysulfuron at higher pH was likely due to greater absorption of trifloxysulfuron at these pH levels.

Trifloxysulfuron accumulation in the above treated leaf section was significant for harvest interval by species interaction. At all harvest intervals Palmer amaranth translocated more  $^{14}\text{C}$ -trifloxysulfuron into above treated leaf sections than Texasweed (Figure 5). Askew and Wilcut (2002) showed that jimsonweed translocated significantly more  $^{14}\text{C}$ -trifloxysulfuron to meristems than cotton, peanut, or sicklepod. Trifloxysulfuron partitioning into roots accounted for less than 2% of recovered  $^{14}\text{C}$  for all pH and species combinations (data not shown). Manley et al. (1999) reported very

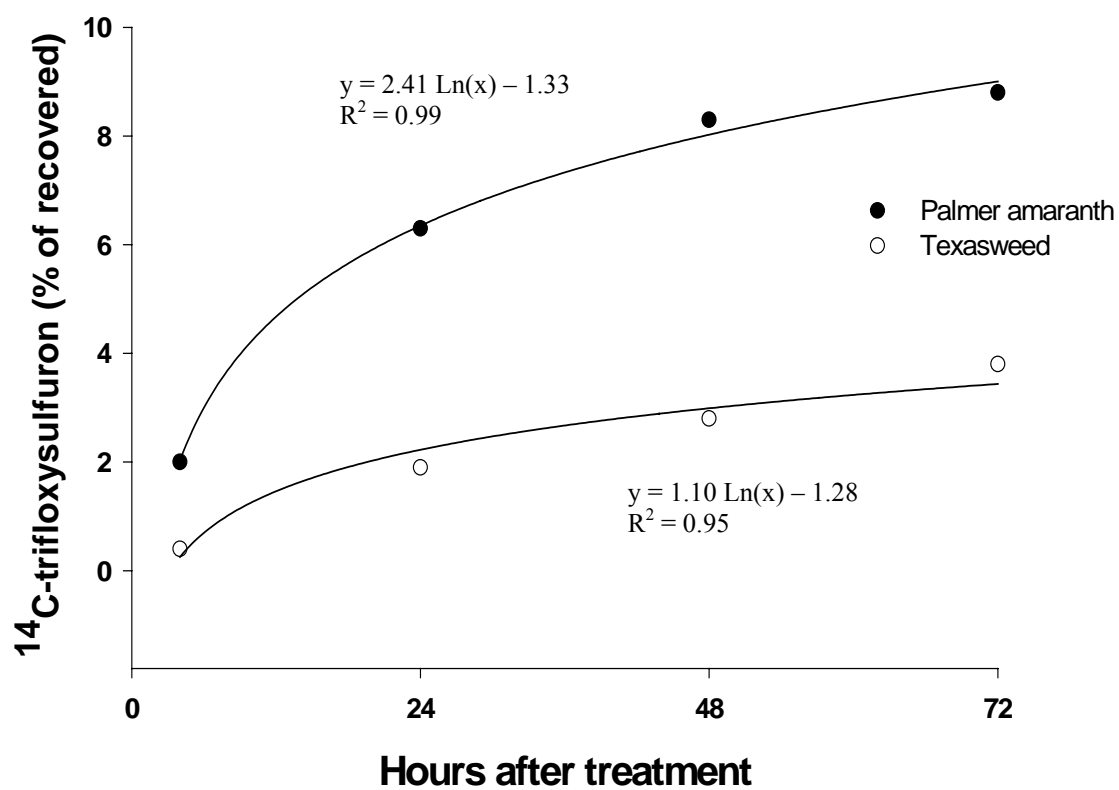


Figure 5. Partitioning of  $^{14}\text{C}$ -trifloxysulfuron in the above treated leaf sections of Palmer amaranth and Texasweed averaged over pH (5, 7, and 9).

limited translocation of nicosulfuron and chlorimuron to roots of smooth pigweed (*Amaranthus hybridus* L.), indicating reduced basipetal translocation.

In summary, acidic spray carrier pH led to decreased absorption of trifloxysulfuron when averaged over harvest interval and species. Additionally, translocation of trifloxysulfuron was reduced by acidic spray carrier pH in Texasweed. These data suggest that increasing the pH of the spray carrier by approximately two pH units above the  $pK_a$  can enhance absorption and translocation of trifloxysulfuron in some weed species as evident in Palmer amaranth and Texasweed. This understanding may potentially lead to a more consistent dose of this material and other SUs with similar chemical characteristics.

**CHAPTER IV**  
**SURFACE RUNOFF LOSSES OF TRIFLOXYSULFURON IN COTTON**  
**(*Gossypium hirsutum* L.)\***

**Introduction**

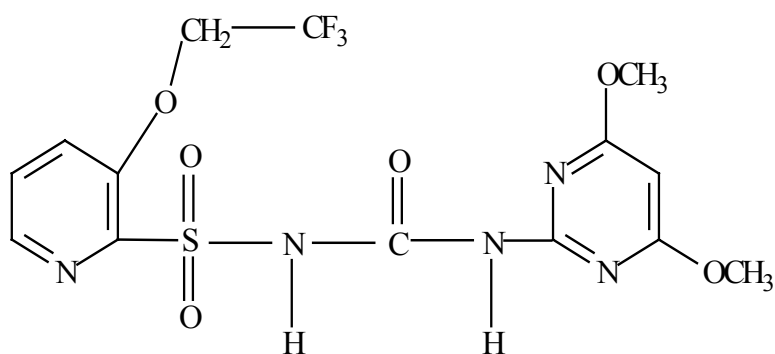
Trifloxysulfuron is a sulfonylurea herbicide (SU) developed for post-emergence weed control in cotton (*Gossypium hirsutum* L.), sugarcane (*Saccharum* spp.) and turfgrass (Holloway et al. 2000; Hudetz et al. 2000). It has an ionizable functional group with a  $pK_a$  of 4.81 (Figure 6). At neutral pH the octanol-water partition coefficient ( $K_{ow}$ ) for trifloxysulfuron is 0.37, and its water solubility is  $5016 \text{ mg L}^{-1}$  (Vencill 2002). Consequently, trifloxysulfuron will be predominately in the anionic form at near-neutral soil pH and should partition primarily into the aqueous phase of the soil solution.

The potential for off-site transport of SUs has been documented in surface water monitoring studies, natural rainfall and simulated rainfall studies. In a large scale monitoring study conducted in the Midwestern United States, 212 water samples were collected from 75 surface-water sites and 25 ground water sites (Battaglin et al. 2000). At least one of the 16 targeted SUs was detected in 83% of the stream samples, 86% of the reservoir samples, and 24% of the ground water samples. In a natural rainfall study, fractional losses of sulfosulfuron were 0.5% when applied post-emergence to winter

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\*Reproduced in part with permission from the Journal of Agricultural and Food Chemistry, Matocha, M.A., L.J. Krutz, S.A. Senseman, K.N. Reddy, M.A. Locke, et al. Foliar washoff potential and surface runoff losses of trifloxysulfuron in cotton, in press. Unpublished work copyright 2006 American Chemical Society.

wheat at 19.8 g a.i. ha<sup>-1</sup> (Brown et al. 2004). In a simulated rainfall study, fractional losses of chlorimuron ethyl and nicosulfuron applied post-emergence at 14 g a.i. ha<sup>-1</sup> to soybean and corn, respectively, did not exceed 2.2% (Afyuni et al. 1997). Fractional losses of sulfometuron-methyl applied at 0.4 kg ha<sup>-1</sup> as either a dispersible granule or an emulsifiable concentrate to a mixed stand of common bermudagrass/bahiagrass and bare plots did not exceed 2.0% for any treatment (Wauchope et al. 1990).



Molecular weight	459.34 g mole <sup>-1</sup>
pKa	4.81
Vapor pressure	<1 x 10 <sup>-7</sup> Pa
Octanol/water coefficient	0.37 (pH 7)

Figure 6. Chemical structure and characteristics of trifloxysulfuron.

## Materials and Methods

### Surface runoff

Surface runoff of trifloxysulfuron was determined in 2.24-m long by 1.22-m wide by 0.25-m deep fiberglass trays with impermeable bottoms. One end of the tray provided a lip over which runoff water flowed into a sloped-floor trough. Trays were supported on concrete block pedestals 30 cm high and were adjusted to 1.2% slope. The soil used in the study was a Dundee silt loam (fine-silty, mixed, active, thermic Typic Endoqualfs). Trays were filled with soil to a depth of 23 cm, and the soil surface was leveled by raking. Four trays were planted with cotton on 91.4 cm rows and four trays were kept bare.

Trifloxysulfuron was applied at  $7.9 \text{ g a.i. ha}^{-1} + \text{NIS}^1$  at 0.25% v/v using a compressed-air tractor mounted sprayer delivering  $187 \text{ L ha}^{-1}$  operating at 241 kPa. Herbicide was applied with 8004 flat fan nozzles at 48 cm approximately 10 min after solution preparation. Trifloxysulfuron application rate was determined by analysis of four 7-cm diameter filter papers (Whatman no. 2) per plot. In bare plots, all four filter papers were attached to the soil surface. In cotton plots, one filter paper was attached to the top leaf of a cotton plant and three were attached to the soil surface. Filter papers were collected 10 min after spray application, placed in 35-mL glass centrifuge tubes, and extracted immediately with 10 mL of acetonitrile. Twenty-four h after herbicide application, simulated rainfall was applied at  $7.5 \text{ cm h}^{-1}$  for 20 min resulting in a nominal application of 2.5 cm of rainfall. Runoff was captured in a holding tank containing a 1.7 Pa pressure transducer, and the runoff rate was determined by recording the water height

in the holding tank with a Campbell Scientific CR-200 electronic data logger<sup>2</sup> at 60-s intervals. At the end of the 20-min simulation, composite samples were collected in 1-L glass jars to determine herbicide and sediment losses.

### **Herbicide and sediment analysis**

Surface runoff samples were vacuum filtered through 0.7- $\mu$ m nominal pore size glass fiber filters<sup>3</sup>. Filtrate (1 L) was fortified with an internal standard (imazethapyr 5  $\mu$ g L<sup>-1</sup>) and acidified to pH  $\leq$  2.7 with 85% phosphoric acid. Acidified samples were solid-phase extracted using 6-mL Oasis HLB cartridges<sup>4</sup> preconditioned with 2 mL of methanol followed by 5 mL of distilled water. Cartridges were washed with 20 mL of methanol: pH 2.0 HPLC-grade water acidified with 85% phosphoric acid (3/7, v/v). Cartridges were eluted with 2 mL of HPLC-grade acetonitrile. Extracts were reduced to approximately 0.7 mL by evaporative concentration under an N<sub>2</sub> gas stream and then brought to 1-mL with HPLC-grade acetonitrile. Total sediment was determined by transferring a 200-mL aliquot of well-shaken runoff into a weighed beaker and weighing the residue remaining in the beaker after oven drying.

### **HPLC Analysis**

Analytes were identified and quantified with a Waters 2695 HPLC separations module with a Waters 996 photodiode array detector. The HPLC was fitted with a 2.1-mm-diameter by 150-mm-length Waters Symmetry C18 column. All solvents were HPLC-grade and mobile phase consisted of acetonitrile and 0.30 mM potassium phosphate buffer at pH 2.7 (4/6,v/v). Buffered mobile phase was adjusted to the proper pH with 85% aqueous phosphoric acid. Mobile phase flow rate was constant at 0.3 mL



min<sup>-1</sup>. Recovery of trifloxysulfuron was  $98.4 \pm 4 \%$ . The instrument limit of detection was  $0.11 \mu\text{g mL}^{-1}$ , and the method limit of quantitation was  $0.33 \mu\text{g L}^{-1}$  (n=14).

### Statistics

Unpaired *t* tests were performed using the data analysis module in Microsoft EXCEL 2000. Since surface runoff studies are inherently highly variable among plots, differences in herbicide losses were evaluated at  $P \leq 0.10$ .

## Results and Discussion

At the time of herbicide application, canopy coverage was 16% and height of cotton was 25.6 cm (Table 8). Since bare plots were maintained vegetation-free by manual hoeing, canopy height and coverage were zero. Herbicide applications were not different among treatments nor did they differ from the nominal application rate. Thus, herbicide losses were calculated based on the nominal application rate of  $7.9 \text{ g ha}^{-1}$ . Hydrological characteristics including rainfall, time to runoff, runoff loss, and runoff rate were not different among treatments.

The average edge-of-field concentration of trifloxysulfuron was greater for cotton plots compared to bare plots (Table 9). Cumulative trifloxysulfuron losses from cotton plots were  $0.21 \text{ g ha}^{-1}$  while losses from bare plots were  $0.13 \text{ g ha}^{-1}$ . These values correspond to fractional losses of 2.7% for cotton plots and 1.7% for bare plots. Fractional losses of trifloxysulfuron from both treatments were in the range of those reported for other SUs including sulfosulfuron, chlorimuron ethyl, nicosulfuron, and sulfometuron-methyl (Afyuni et al. 1997; Brown et al. 2004; Wauchope et al. 1990).

Table 8. Vegetation, soil, rainfall, and hydrologic characteristics of plot area.

Parameter	Units	Bare	Cotton	t-test
Canopy cover	%	0.0	15.7 (1.7)	< 0.0001
Canopy height	cm	0.0	25.6 (0.50)	< 0.0001
Soil moisture	%	18.2 (2.5) <sup>a</sup>	14.9 (1.6)	0.07
Rainfall	cm	2.3 (0.06)	2.4 (0.06)	0.06
Time to runoff	min	3.3 (1.26)	3.8 (0.50)	0.49
Runoff	cm	1.6 (0.19)	1.6 (0.05)	0.58
Runoff rate	L min <sup>-1</sup>	2.7 (0.13)	2.8 (0.13)	0.30
Sediment loss	kg ha <sup>-1</sup>	1499 (403)	1051 (258)	0.11

<sup>a</sup> Numbers in parentheses indicate one standard deviation.

Table 9. Measured application rates, average edge-of-field concentrations, mass lost and fraction lost of trifloxysulfuron applied to bare soil plots and cotton plots.

Observation	Units	Bare	Cotton	<i>t</i> -test
Mass applied	g ha <sup>-1</sup>	8.0 (1.15) <sup>a</sup>	7.8 (1.81)	0.81
Concentration	µg L <sup>-1</sup>	0.8 (0.12)	1.33(0.16)	0.05
Mass lost	g ha <sup>-1</sup>	0.1 (0.05)	0.2 (0.05)	0.07
Fraction lost	%	1.7 (0.55)	2.7 (0.55)	0.07

<sup>a</sup> Numbers in parentheses indicate one standard deviation.

Greater loss of trifloxysulfuron from cotton plots was likely due to foliar washoff. Once washed off the cotton foliage, trifloxysulfuron would be available for sorption to soil, leaching, and/or transport in surface runoff. Sorption of washed off trifloxysulfuron to soil during the 20-min rainfall simulation would be minimal, but a large fraction of the herbicide would be available for leaching and/or surface runoff. Similarly, losses of imazaquin from plots with 100% pigweed cover were 23% compared to 16% for bare plots (Reddy and Locke 1996).

Rainfall simulation data indicated that fractional losses of trifloxysulfuron applied to cotton at the 5-leaf stage did not exceed 3%. However, losses of trifloxysulfuron were greater from cotton plots compared to bare plots. Thus, losses of trifloxysulfuron may be minimized if applied to cotton at or soon after the 5-leaf stage when canopy closure is minimal and when rainfall is not imminent.

## **CHAPTER V**

### **SUMMARY AND CONCLUSIONS**

The first study quantified the dissipation of spray solutions of trifloxysulfuron at three pH levels in a simulated spray tank after 0, 1, 3, 7, 14, and 21 d. Resulting mixtures were also evaluated for efficacy on Palmer amaranth. Herbicide dissipation was most rapid under acidic conditions with little or no difference between neutral and alkaline pH levels. All pH levels and periods of incubation resulted in significant dry weight reductions on treated Palmer amaranth compared to the untreated. Correlation coefficients showed a lack of correlation between percent dry weight reduction and percent remaining in solution at pH 9.

Data from the absorption and translocation study showed absorption of trifloxysulfuron was greater for Palmer amaranth than for Texasweed when averaged over time and pH. Altering pH did not affect the translocation of trifloxysulfuron in Palmer amaranth. In contrast, translocation of  $^{14}\text{C}$ -trifloxysulfuron in Texasweed increased in the order of  $\text{pH } 5 < \text{pH } 7 = \text{pH } 9$ . Acidic spray carrier pH led to decreased absorption of trifloxysulfuron when averaged over harvest interval and species. These data suggest that increasing the pH of the spray carrier by approximately two pH units above the pKa can enhance absorption and translocation of trifloxysulfuron in some weed species.

Surface runoff losses of trifloxysulfuron applied to cotton showed greater cumulative trifloxysulfuron losses in runoff from cotton plots compared to bare plots.

Runoff values correspond to fractional losses of 2.7% for cotton plots and 1.7% for bare plots. Greater loss of trifloxysulfuron from cotton plots was likely due to foliar washoff. Once washed off the cotton foliage, trifloxysulfuron would be available for sorption to soil, leaching, and/or transport in surface runoff.

These studies provide important information regarding the stability, plant uptake, and runoff potential of trifloxysulfuron. Acidic spray carrier pH led to more rapid dissipation and less reduction in Palmer amaranth dry weights as a percent of untreated. The acidic pH also led to decreased absorption of  $^{14}\text{C}$ -trifloxysulfuron when averaged over time and species. Runoff data showed greater runoff from cotton plots compared to bare plots. Perhaps mixing trifloxysulfuron with an alkaline buffer solution would provide the most stable and efficacious alternative. Improper spray carrier pH could lead to decreased absorption into plants as well as increased foliar washoff and potential surface runoff from agricultural fields.

## LITERATURE CITED

- Afyuni, M.M., M.G. Waggoner, and R.B. Leidy. 1997. Runoff of two sulfonylurea herbicides in relation to tillage system and rainfall intensity. *J. Environ. Qual.* 26:1318-1326.
- Askew, S.D. and J.W. Wilcut. 2002. Absorption, translocation, and metabolism of foliar-applied trifloxysulfuron in cotton, peanut, and selected weeds. *Weed Sci.* 50:293-298.
- Battaglin, W.A., E.T. Furlon, M.R. Burkhardt, and C.J. Peter. 2000. Occurrence of sulfonylurea, sulfonamide, imidazolinone, and other herbicides in rivers, reservoirs and ground water in the Midwestern United States, 1998. *Sci. Total Environ.* 248:123-133.
- Berger, B.M. and N.L. Wolfe. 1996. Hydrolysis and biodegradation of sulfonylurea herbicides in aqueous buffer systems and anaerobic water-sediment systems: Assessing fate pathways using molecular descriptors. *Environ. Toxicol. Chem.* 15:1500-1507.
- Berglof, T., W.C. Koskinen, M.J. Duffy, K.A. Norberg, and H. Kylin. 2003. Metsulfuron methyl sorption-desorption in field-moist soils. *J. Agric. Food Chem.* 51:3598-3603.
- Branson, J.W., K.L. Smith, and J.L. Barrentine. 2005. Comparison of trifloxysulfuron and pyriproxyfen in glyphosate-resistant and bromoxynil-resistant cotton. *Weed Technol.* 19:404-410.

- Braschi, I., L. Calamai, M.A. Cremonini, P. Fusi, C. Gessa, O. Pantani, and A. Pusino. 1997. Kinetics and hydrolysis mechanism of triasulfuron. *J. Agric. Food Chem.* 45:4495-4499.
- Braschi, I., A. Pusino, C. Gessa, and J.M. Bollag. 2000. Degradation of primisulfuron by a combination of chemical and microbiological processes. *J. Agric. Food Chem.* 48:2565-2571.
- Brown, C.D., I.G. Dubus, P. Fogg, M. Spirlet, and C. Gustin. 2004. Exposure to sulfosulfuron in agricultural drainage ditches: Field monitoring and scenario-based modeling. *Pestic. Manage. Sci.* 60:765-776.
- Burke, I.C. and J.W. Wilcut. 2004. Weed management in cotton with CGA-362622, fluometuron, and pyriithiobac. *Weed Technol.* 18:268-276.
- Camacho, R.F. and L.J. Moshier. 1991. Absorption, translocation, and activity of CGA-136872, DPX-V9360, and glyphosate in rhizome Johnsongrass (*Sorghum halpense*). *Weed Sci.* 39:354-357.
- Carey, J.B., D. Penner, and J.J. Kells. 1997. Physiological basis for nicosulfuron and primisulfuron selectivity in five plant species. *Weed Sci.* 45:22-30.
- Gillespie, G.R. 1994. Basis for the differential response of quackgrass (*Elytrigia repens*) biotypes to rimsulfuron. *Weed Sci.* 42:8-12.
- Green, J.M. and W.R. Cahill. 2003. Enhancing the biological activity of nicosulfuron with pH adjusters. *Weed Sci.* 17:338-345.



- Holloway, J.C., Jr., J.W. Wells, M. Hudetz, W. Bachman, G. Cloud, et al. 2000. CGA-362622 application timing, rates, and weed spectrum in cotton. *Proc. South. Weed Sci. Soc.* 53:240.
- Hudetz, M., W. Foery, J. Wells, and J.E. Soares. 2000. CGA 362622, a new low rate Novartis post-emergent herbicide for cotton and sugarcane. *Proc. South. Weed Sci. Soc.* 53:163-166.
- Hultgren, R.P., R.J.M. Hudson, and G.K. Sims. 2002. Effects of soil pH and soil water content on prosulfuron dissipation. *J. Agric. Food Chem.* 50:3236-3243.
- Koger, C.H., K.N. Reddy, and D.H. Poston. 2004. Factors affecting seed germination, seedling emergence, and survival of Texasweed (*Caperonia palustris*). *Weed Sci.* 52:989-995.
- Koger, C. H., A. J. Price, and K. N. Reddy. 2005. Weed control and cotton response to combinations of glyphosate and trifloxysulfuron. *Weed Technol.* 19:113-121.
- Liu, Z.Q. 2002. Lower formulation pH does not enhance bentazone uptake in to plant foliage. *New Zealand Plant Prot.* 55:163-167.
- Manley, B.S., K.K. Hatzios, and H.P. Wilson. 1999. Absorption, translocation, and metabolism of chlorimuron and nicosulfuron in imidazolinone-resistant and susceptible smooth pigweed (*Amaranthus hybridus*). *Weed Technol.* 13:759-764.
- Matocha, M.A., L.J. Krutz, S.A. Senseman, K.N. Reddy, M.A. Locke, et al. 2006. Foliar washoff potential and surface runoff losses of trifloxysulfuron in cotton. *J. Agric. Food Chem.* *In Press*.

- Matocha, M.E. and P.A. Baumann. 2004. Texasweed management in Texas cotton. Proc. Texas Plant Prot. Conf. 16:26.
- McElroy, J.S., F.H. Yelverton, I.C. Burke, and J.W. Wilcut. 2004. Absorption, translocation, and metabolism of halosulfuron and trifloxysulfuron in green kyllinga (*Kyllinga brevifolia*) and false green kyllinga (*K. gracillima*). Weed Sci. 52:704-710.
- McIntosh, M.S. 1983. Analysis of combined experiments. Agron. J. 75:153-155.
- Mersie, W. and C.L. Foy. 1986. Adsorption, desorption, and mobility of chlorsulfuron in soils. J. Agric. Food Chem. 34:89-82.
- Moberg, W. K. and B. Cross. 1990. Herbicides inhibiting branched-chain amino acid biosynthesis. Pestic. Sci. 29:241-246.
- Morgan, G.D., P.A. Baumann, and J.M. Chandler. 2001. Competitive impact of Palmer amaranth (*Amaranthus palmeri*) on cotton (*Gossypium hirsutum*) development and yield. Weed Technol. 15:408-412.
- Morrica, P., F. Barbato, A. Giordano, S. Seccia, and F. Ungaro. 2000. Adsorption and desorption of imazosulfuron by soil. J. Agric. Food Chem. 48:6132-6137.
- Morrica, P., F. Barbato, R.D. Iacovo, S. Seccia, and F. Ungaro. 2001. Kinetics and mechanism of imazosulfuron hydrolysis. J. Agric. Food Chem. 49:3816-3820.
- Porterfield, D., J.W. Wilcut, and S.D. Askew. 2002. Weed management with CGA-362622, fluometuron, and prometryn in cotton. Weed Sci. 50:642-647.

- Porterfield, D., J. W. Wilcut, J. W. Wells, and S. B. Clewis. 2003. Weed management with CGA-362622 in transgenic and nontransgenic cotton. *Weed Sci.* 51:1002-1009.
- Pusino, A., M.G. Fiori, I. Braschi, and C. Gessa. 2003. Adsorption and desorption of triasulfuron by soil. *J. Agric. Food Chem.* 51:5350-5354.
- Pusino, A., M. V. Pinna, and C. Cessa. 2004. Azimsulfuron sorption-desorption on soil. *J. Agric. Food Chem.* 52:3462-3466.
- Reddy, K.N., M.A. Locke, S.C. Wagner, R.M. Zablotowicz, L.A. Gaston, and R.J. Smeda. 1995. Chlorimuron ethyl sorption and desorption kinetics in soils and herbicide-desiccated cover crop residues. *J. Agric. Food Chem.* 43:2752-2757.
- Reddy, K.N. and M.A. Locke. 1996. Imazaquin spray retention, foliar washoff and runoff losses under simulated rainfall. *Pestic. Sci.* 48:179-187.
- Reddy, K.N. and M.A. Locke. 1998. Sulfentrazone sorption, desorption, and mineralization in soils from two tillage systems. *Weed Sci.* 46:494-500.
- Richardson, R. J., H. P. Wilson, G. R. Armel and T. E. Hines. 2004. Mixtures of glyphosate with CGA 362622 for weed control in glyphosate-resistant cotton (*Gossypium hirsutum*). *Weed Technol.* 18:16-22.
- Saha, S. and G. Kulshrestha. 2002. Degradation of sulfosulfuron, a sulfonylurea herbicide, as influenced by abiotic factors. *J. Agric. Food Chem.* 50:4572-4575.
- Sarmah, A.K. and J. Sabadie. 2002. Hydrolysis of sulfonylurea herbicides in soils and aqueous solutions: A review. *J. Agric. Food Chem.* 50:6253-6265.

- Schneiders, G.E., M.K. Koeppe, M.V. Naidu, P. Horne, A.M. Brown, and C.F. Mucha. 1993. Fate of rimsulfuron in the environment. *J. Agric. Food Chem.* 41:2404-2410.
- Smith, D.T., R.V. Baker, and G.L. Steele. 2000. Palmer amaranth (*Amaranthus palmeri*) impacts on yield, harvesting, and ginning in dryland cotton (*Gossypium hirsutum*). *Weed Technol.* 14:122-126.
- Sterling, T.M. 1994. Mechanisms of herbicide absorption across plant membranes and accumulation in plant cells. *Weed Sci.* 42:263-276.
- Troxler, S.C., I.C. Burke, J.W. Wilcut, W.D. Smith, and J. Burton. 2003. Absorption, translocation, and metabolism of foliar-applied trifloxysulfuron in purple and yellow nutsedge (*Cyperus rotundus* and *C. esculentus*). *Weed Sci.* 51:13-18.
- Vega, D. J.P. Cambon, and J. Bastide. 2000. Triflurosulfuron-methyl dissipation in water and soil. *J. Agric. Food Chem.* 48:3733-3737.
- Vencill V.K. 2002. *Herbicide Handbook*, Eighth edition, Champaign, IL: Weed Science Society of America, 493 pp.
- Vicari, A., Zimdahl, R.L., Cranmer, B.K., and Dinelli, G. 1996. Primisulfuron and rimsulfuron degradation in aqueous solution and adsorption in six Colorado soils. *Weed Sci.* 44:672-677.
- Wauchope, R.D., R.G. Williams, and L.R. Marti. 1990. Runoff of sulfometuron-methyl and cyanazine from small plots: Effects of formulation and grass cover. *J. Environ. Qual.* 19:119-125.

- Whisenant, S.G. and R.W. Bovey. 1993. Water quality effects on stability and phytotoxicity of picloram and clopyralid. *J. Range Manage.* 46:254-256.
- Wilcut, J.W., G.R. Wehtje, M.G. Patterson, T.A. Cole, and T.V. Hicks. 1989. Absorption, translocation, and metabolism of foliar-applied chlorimuron in soybeans (*Glycine max*), peanut (*Arachis hypogaea*), and selected weeds. *Weed Sci.* 37:175-180.
- Wilcut, J.W., S.D. Askew, and D. Porterfield. 2000. Weed management in non-transgenic and transgenic cotton with CGA 362622. *Proc. South. Weed Sci. Soc.* 53:27.

## **APPENDIX A**

### **SOURCES OF MATERIALS**

#### **Chapter II**

<sup>1</sup>Varian pH Meter. Varian, Inc. Palo Alto, CA 94304.

<sup>2</sup> Induce<sup>®</sup> nonionic low foam wetter-spreader adjuvant contains 90% nonionic surfactant (alkylarylpolyoxyalkane ether isopropanol), free fatty acids, and 10% water, Helena Chemical Company, Suite 500, 6075 Poplar Avenue, Memphis, TN 38137.

#### **Chapter III**

<sup>1</sup>Jiffy mix, Jiffy Products of America Inc., 951 Swanson Drive, Batavia, IL 60510.

<sup>2</sup>Induce<sup>®</sup> nonionic low foam wetter-spreader adjuvant contains 90% nonionic surfactant (alkylarylpolyoxyalkane ether isopropanol), free fatty acids, and 10% water, Helena Chemical Company, Suite 500, 6075 Poplar Avenue, Memphis, TN 38137.

<sup>3</sup> Ecolume, ICN, 330 Hyland Avenue, Costa Mesa, CA 92626.

<sup>4</sup>Tri-carb 2500TR Liquid Scintillation Analyzer, Packard BioScience Company, 800 Research Parkway, Downers Grove, IL 60515.

<sup>5</sup> Kimwipes EX-L, Kimberly-Clark Corporation, 1400 Holcomb Bridge Road, Roswell, GA 30076.

<sup>6</sup> Packard Oxidizer 306, Packard Instruments Company, 2200 Warrenville Road, Downers Grove, IL 60515.

## **Chapter IV**

<sup>1</sup>Induce<sup>®</sup> nonionic low foam wetter-spreader adjuvant contains 90% nonionic surfactant (alkylaryl polyoxyalkane ether isopropanol), free fatty acids, and 10% water, Helena Chemical Company, Suite 500, 6075 Poplar Avenue, Memphis, TN 38137.

<sup>2</sup>Campbell Scientific Inc., Logan, UT.

<sup>3</sup>Fisherbrand, Pittsburgh, PA.

<sup>4</sup>Waters, Milford, MA.

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